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Contract N00014-89-J-1041  
R&T Code 413C012-04

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JUN 4 1992  
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Technical Report No. 18

Reactions of Polymers with Pendant Cyclophosphazenes

by

C.W. Allen, K.R. Carter, M. Bahadur and D.E. Brown

Prepared for Publication

in

Polymer Preprints

May 22, 1992

University of Vermont  
Department of Chemistry  
Burlington, VT 05405-0125

92-14367



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## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			Available for public release; distribution unlimited		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of Vermont			6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION ONR
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Vermont Burlington, VT 05405-0125			7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 North Quincy Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. N00014-89	PROJECT NO. J-1041	TASK NO. 413C012
11. TITLE (Include Security Classification) Reactions of Polymers with Pendant Cyclophosphazenes					
12. PERSONAL AUTHOR(S) C.W. Allen, K.R. Carter, M. Bahadur and D.E. Brown					
13a. TYPE OF REPORT Reprint		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day)	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION Prepared for publication in "Polymer Preprints"					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	cyclophosphazenes redox polymers		
			polymer reactions		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The reactions poly(pentachlorovinylloxycyclotriphosphazene), with a variety of amines and oxyanions have been examined. Variable degrees of substitution are obtained and the resulting materials have a complex thermal decomposition process. Copolymers having alkynyl phosphazene side chains react with dicobalt octacarbonyl to form redox active polymers.</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

# REACTIONS OF POLYMERS WITH PENDANT CYCLOPHOSPHAZENES

C.W. Allen, K.R. Carter, M. Bahadur and D.E. Brown

Department of Chemistry  
University of Vermont  
Burlington, VT 05405-0125

## INTRODUCTION

One significant area of interest in the study of hybrid inorganic/organic polymers has been that of chemical reactivity. The ability to effect property modification and/or incorporation of new, useful functionalities via reactions of preformed polymers provides an incentive for pursuit of these studies. The reactions of poly(dichlorophosphazene),  $(\text{NPCl}_2)_n$ , which have been explored by Allcock and coworkers,<sup>1</sup> are arguably the most extensive for any polymer system. Synthetic transformations of  $(\text{NPCl}_2)_n$  with structurally simple units such as fluoroalkoxides gives elastomers with low Tg values while more complex substituents can provide sites for biological or catalytic activity.<sup>1</sup> We have been examining an alternative type of phosphazene polymer in which cyclophosphazenes<sup>2</sup> are substituents on a linear hydrocarbon chain.<sup>2</sup> In this paper we report some approaches to applying the wide variety of reactions which have been carried out on cyclophosphazenes to reactions of cyclophosphazenes in a polymeric environment.

## EXPERIMENTAL

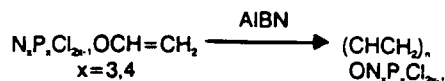
**Materials.** Hexachlorocyclotriphosphazene,  $\text{N}_3\text{P}_3\text{Cl}_6$  (Nippon Soda) was converted to  $\text{N}_3\text{P}_3\text{F}_6$ .<sup>4</sup> Previously reported procedures were used for preparation of  $\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{H}_5$ ,  $\text{N}_3\text{P}_3\text{Cl}_3\text{OCH}=\text{CH}_2$ ,<sup>4</sup> and  $[\text{CH}(\text{ON}_3\text{P}_3\text{Cl}_2)\text{CH}_2]_n$  (I).<sup>4</sup> **Measurements.** Gel permeation chromatography was performed on a Waters 202 high pressure liquid chromatograph equipped with  $10^4$  and  $10^5$  Å microstysragel columns. Thermal analyses were carried out using a Perkin-Elmer TGS-2 thermogravimetric system interfaced with a PETOS thermal analysis data station. Cyclic voltammetry measurements were performed on 0.5mM solutions with  $\text{Bu}_4\text{NPF}_6$  as supporting electrolyte and SCE reference electrode using a Princeton Applied Research model 273 potentiostat.

**Syntheses.** Derivatives of  $\text{N}_3\text{P}_3\text{Cl}_3\text{OCH}=\text{CH}_2$  were prepared by reactions of stoichiometric amounts of the appropriate nucleophile followed by chromatographic purification. Products of reactions of various nucleophiles with the polymer,  $[\text{CH}(\text{ON}_3\text{P}_3\text{Cl}_2)\text{CH}_2]_n$ , were isolated by precipitation with methanol except for the methylamino derivative which was isolated by filtration of the precipitated polymer.

The reaction of 4-(1-methylethenyl)phenyl lithium<sup>7</sup> with  $\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{H}_5$  yields  $2,4\text{-N}_3\text{P}_3\text{F}_6(\text{C}_6\text{H}_4)[(\text{C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{CH}_2)]_n$  which undergoes facile copolymerization with styrene using azobis(isobutyronitrile) (AIBN) as an initiator. Reactions of  $\text{CO}_2(\text{CO})_2$  with solutions of this copolymer yields the cobalt carbonyl complex  $[\text{CH}(\text{Ph})\text{CH}_2][\text{C}(\text{CH}_3)(\text{N}_3\text{P}_3\text{F}_6\text{C}_6\text{H}_4\text{Co}_2(\text{CO})_2)\text{CH}_2]_n$ .

## RESULTS AND DISCUSSION

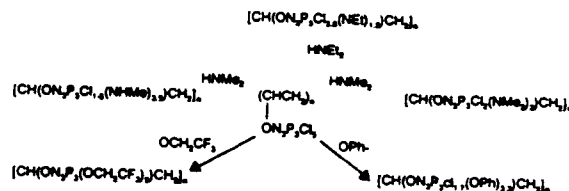
The polymerization of the vinyloxycyclotri-<sup>2</sup> and tetraphosphazenes leads to highly functionalized polymers with five and seven reactive sites per monomer unit respectively.



Copolymerization of the trimeric and tetrameric derivatives leads to polymers with both six and seven membered rings as substituents. These polymers undergo a remarkable set of thermal decomposition reactions. The first step is a cross linking process wherein the cyclophosphazene serves as the bridging unit between two chains by way of carbon-phosphorus bond formation accompanied by HCl release. The fact that this process occurs at relatively mild conditions suggests the possibility of utilization of the chlorocyclophosphazene unit in thermosetting polymers. The second step, which occurs at much higher temperatures ( $>400^\circ\text{C}$ ), involves elimination of the oxobridged dimers,  $(\text{N}_3\text{P}_3\text{Cl}_2)_2\text{O}$ .

There are two basic routes to chemical modification of the poly(vinyloxycyclophosphazenes): derivatization of the monomer followed by polymerization or derivatization of the performed polymer. We have previously shown that strongly electron donating substituents will produce vinyloxycyclophosphazene monomers that do not undergo radical chain homopolymerization.<sup>7</sup> Since weakly electron donating or electron withdrawing substituents will allow for polymerization, we examined the polymerization of  $2,4\text{-N}_3\text{P}_3\text{Cl}_3(\text{OCH}_2\text{CF}_3)_2\text{OCH}=\text{CH}_2$ ,  $2,4,6\text{-N}_3\text{P}_3\text{Cl}_3(\text{OCH}_2\text{CF}_3)_3\text{OCH}=\text{CH}_2$  and  $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_6\text{OCH}=\text{CH}_2$ . In each case, polymerization of the neat liquid monomer (using AIBN as an initiator) proceeded smoothly to give polymers with a broad spectrum of solubility. However, the molecular weights (GPC) in the series  $[\text{CH}(\text{ON}_3\text{P}_3\text{Cl}_2)(\text{OCH}_2\text{CF}_3)_x\text{CH}_2]_n$  ( $x=1,2,5$ ) decrease significantly with increasing trifluoroethoxide substitution. This observation indicates chain transfer events involving the trifluoroethoxy substituents and suggests the need to explore the alternative method for producing substituted vinyloxycyclophosphazene polymers.

The reactions of I with various nucleophiles has been explored and the synthetic results are summarized in Scheme 1.

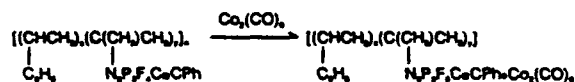


Scheme 1

The trifluoroethoxide derivative is a high molecular weight material with all chlorine atoms in the parent polymer (I) being replaced. Thermal decomposition of this polymer follows a simple random scission process while the partially substituted materials undergo the two step process described for I. The reactions of the remaining chlorine atoms in I. This behavior is more like that of the cyclophosphazenes, where reactions are more difficult at high degrees of substitution,<sup>3</sup> than corresponding reactions of poly(dichlorophosphazene).<sup>1</sup> The thermal decomposition behavior also varies in the series of polymers described in Scheme 1. Some follow the two step process seen in I while others produce a much higher char level. In the phenoxy derivative, over 50% of a phosphazene containing (as indicated by IR spectroscopy) char is obtained. A dramatic illustration of simple property modification is seen in the relative solubilities of the methylamino and trifluoroethoxy derivatives where the former is only soluble in water or methanol and the later is soluble in most solvents with the exception of water and methanol.

Another approach to derivatization of pendant cyclophosphazenes is to work with substituents which can be transformed into more complex units. We have been interested in the reactions of alkynyl phosphazenes with organometallic reagents.<sup>9</sup> As an example of this approach, we have prepared the dicobalt hexacarbonyl derivatives,  $N_2P_2F_6(C\equiv CPh)_2[Co_2(CO)_4]_2$  ( $x=1,2$ ) and reduced them to radical anions.<sup>9</sup> An analogous polymeric system can be prepared using copolymerization chemistry.<sup>10</sup> Reactions of

AIBN



the copolymer with dicobalt octacarbonyl produces the desired organometallic derivative which undergoes reversible electrochemical reduction to the radical anion.

The studies shown above demonstrate the broad range of reactivity and property modification available via the reactions of polymers with pendant cyclophosphazenes.

#### ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research. The gift of  $N_2P_2Cl_4$  from Nippon Soda is appreciated.

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